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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide

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The invention relates to a process for the hydrogenation of carbon monoxide in the presence of an iron catalyst.

It is known that in the catalytic hydrogenation of carbon monoxide, primary products may be obtained which differ largely both in their chemical nature and in their boiling ranges. This variety of products is obtained by varying the synthesis conditions, particularly with respect to the pressure, temperature, gas throughput and gas recycling, as well as by using catalysts of different composition and catalysts which have been prepared by different methods. For iron catalysts, these conditions are very characteristic. In general, a catalyst of a given composition which has been prepared by a given method results in the main, in the formation of synthesis products of a certain composition. For the production of primary products having a high content of oxygen-containing organic compounds strongly alkalized iron catalysts are known to be useful.

It is known that the inner surface area of catalysts is of decisive importance for their efficiency, particularly with respect to the chemical nature and the boiling range of the primary products. (Reference is made to the work of Tramm "Zur Technik der Kohlenoxydhydrierung", published in "Erdoel und Kohle", Vol. 5 pp. 10—17, particularly Figure 9 and the left-hand column of page 14, and in "Brennstoff-Chemie", Vol. 33, pp. 21—30, particularly page 27, left-hand column, Figure 9).

It has now been found that by the use of a catalyst of a given composition prepared by a given method and thus having a certain surface area, primary products having a high content of hydrocarbons boiling in the gasoline range may be obtained in the hydrogenation of carbon monoxide.

According to the invention, a process for the catalytic hydrogenation of carbon monoxide comprises passing a gas mixture containing hydrogen and carbon monoxide in synthesis proportions over an iron-containing catalyst, which is unsupported or which contains only a small quantity of supporting material, at a temperature in the range 175—300° C., at an elevated pressure of up to 100 atmospheres gauge, and at a rate of from 200 to 1000 volumes of fresh synthesis gas per volume of catalyst per hour, the iron in the catalyst having been obtained by precipitation from a solution of an iron salt at a *p*H value in the range 6.8—7.5, the catalyst having an SiO_2 content of from 5% to 15% obtained by direct impregnation with an alkali metal silicate, and having an alkali content (calculated at K_2O) of from 2% to 6%, the SiO_2 and K_2O contents being by weight and relative to the total iron content of the catalyst, the catalyst having an inner surface area of from 180—230 square metres per gram of the total iron in the catalyst, the catalyst having been reduced prior to use to convert from 10% to 50% of the total iron into the elementary or metallic state.

Where the catalyst is supported, the small quantity of supporting material may, for example, constitute up to 10% by weight of the catalyst. Kieselguhr, alumina, bauxite and asbestos are examples of suitable supporting materials. When used, the supporting material may be suspended in the solution of the iron salt or in the solution of the precipitant prior to the precipitation, or it may be added during the process of precipitation. It is preferred, however, to add the supporting material, when used, to the solution immediately the precipitation of the iron has been completed.

One or more promoters such as copper, silver, lime and metals of the 5th to 7th groups of the periodic system may be incorporated in the catalyst.

The alkali content of the catalyst is preferably in the range 3—4%, and the inner sur-

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face area of the catalyst is preferably from 200 to 230 square metres per gram of the total iron in the catalyst. The catalyst is reduced in known manner prior to use in the synthesis, and it is preferred that from 20% to 30% of the total iron in the catalyst should be in elementary form prior to use in the synthesis.

The alkali metal content of the catalyst may be provided in part by the precipitant used for the precipitation of the iron catalyst, the washing of the precipitated mass being then limited to permit some of the alkali metal compound or compounds to remain in the precipitate. Alternatively, the precipitate may be washed substantially free from alkali-metal compounds, the alkali content of the catalyst being then introduced upon impregnation with an alkali metal silicate to give the catalyst the desired content of SiO_2. Any excess of alkali thereby introduced into the catalyst may be removed by means of dilute nitric acid. Thus the desired content of SiO_2 may be introduced by impregnation of the precipitate with a commercial alkali-metal silicate having, for example, a ratio of alkali-metal (expressed as K_2O) to SiO_2 of 1:2.5 by weight. It will be understood when the alkali metal in the catalyst or in the silicate is not potassium, the alkali metal is expressed as the equivalent of K_2O. The silicic acid (SiO_2) remains quantitatively in the precipitated catalyst mass and cannot be or is not removed therefrom by any chemical step employed in the course of the production of the catalyst. If necessary, the amount of alkali-metal compounds in the catalyst is lowered by means of nitric acid to bring the alkali content within the stipulated range.

The $K_2O:SiO_2$ ratio in the catalyst is advantageously adjusted to a value of from 1:1 to 1:5 by weight. Such a ratio will give particularly favourable results with respect to the life and activity of the catalyst. To obtain a ratio of 1: more than 2.5, the catalyst mass impregnated with the solution of alkali-metal silicate, for example, waterglass, is neutralised with dilute nitric acid while maintaining a *p*H value of 6.5—8, thereby dissolving out a more or less large proportion of the alkali-metal and shifting the ratio $K_2O:SiO_2$ in favour of the silicic acid (SiO_2).

If a $K_2O:SiO_2$ ratio of 1: less than 2.5 is desired, the washing of the precipitated catalyst mass is advantageously effected to leave a residual alkali metal content of 1—2% (calculated as K_2O and based on the weight of the total content of iron). By the subsequent direct impregnation with the alkali-metal silicate, it is possible to obtain $K_2O:SiO_2$ ratios which are lower than 1:2.5, such, for example, as 1:1.5 or even 1:1.

The desired content of free iron in the catalyst is obtained by the use of suitable reduction conditions. The reduction is effected with gases containing hydrogen and/or carbon monoxide at temperatures within the range 175°—320° C., and preferably at temperatures between 200° C. and 250° C. A high gas velocity of, for example, 1—2 metres per second and preferably 1.2—1.5 metres per second (calculated at room temperature and at normal atmospheric pressure) has been found to be advantageous.

The inner surface area of the catalyst is a function (a) of the alkali content, (b) of the SiO_2 content, and (c) of the quantity of the total iron which is in the elementary state. The determination of the inner surface area of the catalyst is effected by the preparation of an adsorption isotherm and its evaluation by the method of Brunauer, Emmet and Teller (the so-called BET method). The apparatus required consists substantially of a graduated burette in which the volume of the gas to be adsorbed, such as nitrogen or argon, is measured, a manometer for the determination of the gas pressure, and a small flask in which the adsorbing substance to be tested is placed.

The space velocity or throughput of the fresh synthesis gas is within the range 200 to 1000 volumes per volume of catalyst per hour, and is preferably within the range 200—750 volumes. The primary products obtained in the synthesis have a high content of hydrocarbons boiling in the gasoline range.

The invention is illustrated in the following example:—

EXAMPLE

A boiling aqueous solution which contained 45 grams of Fe, 0.45 grams of Cu and 2.5 grams of CaO in solution in the form of nitrates was added within 2 minutes to a boiling aqueous solution of sodium carbonate so that the *p*H value upon termination of the precipitation was 7.1. The mixture was then heated for a few minutes and immediately thereafter was filtered in the hot state. The filtered mass was washed with hot distilled water so that the residual alkali content, calculated as K_2O and based on the total iron content, in the precipitate was 0.6% by weight.

The moist, precipitated catalyst mass was cooled and impregnated with an aqueous solution of potassium silicate of a concentration of 20% and having a $K_2O:SiO_2$ ratio of 1:2.5 by weight to give the impregnated catalyst mass a total alkali content (calculated as K_2O) of 3.6% by weight of the total iron in the mass. The content of silicic acid (SiO_2) in the mass was 7.8% by weight of the total amount of iron.

The impregnated mass was dried at a temperature of 110° C., crushed and sieved to a grain size of between 2 mm. and 4 mm.

The granulated catalyst mass was reduced for 60 minutes at a temperature of 250° C. with a gas mixture consisting of 75% of hydrogen and 25% of nitrogen using a superficial gas velocity of 1.4 metres per second (calculated at room temperature and at normal atmospheric pressure). 26% of the total iron in the reduced catalyst was in the elementary state.

4.8 litres of the reduced catalyst mass were charged into a double-tube reaction vessel consisting of two concentric tubes, the catalyst being disposed in the annular space between the two tubes whilst a heat transfer medium was passed through the inner tube. Water gas was then contacted with the catalyst at a synthesis pressure of 30 atmospheres gauge and at a temperature of 212° C. at a rate of 500 volumes of fresh gas per volume of catalyst per hour and with the use of a recycle ratio of 2.5:1 (2.5 volumes of recycle gas per volume of fresh gas). The $CO:H_2$ ratio in the water gas was 1:1.19.

The $CO+H_2$ conversion was 61.5%, the methane formation being 7%. The quantity of high boiling hydrocarbons contained in the reaction product was only 35% of the total liquid product.

What we claim is:—

1. A process for the catalytic hydrogenation of carbon monoxide, which comprises contacting a gas mixture containing hydrogen and carbon monoxide in synthesis proportions with an iron-containing catalyst which is unsupported or which contains only a small quantity of supporting material, at a temperature in the range 175°—300° C. at an elevated pressure not exceeding 100 atmospheres gauge and at a rate of from 200 to 1000 volumes of fresh synthesis gas per volume of catalyst per hour, the iron in the catalyst having been obtained by precipitation from a solution of an iron salt at a *p*H value in the range of 6.8—7.5, the catalyst having an SiO_2 content of from 5% to 15% obtained by direct impregnation with an alkali-metal silicate, and having an alkali content (calculated as K_2O) of from 2% to 6%, the SiO_2 and the K_2O contents being by weight and relative to the total iron content of the catalyst, the catalyst having an inner surface area of from 180—230 square metres per gram of the total iron in the catalyst and having been reduced prior to use to convert from 10% to 50% of the total iron into the elementary state.

2. A process according to claim 1, in which the gas throughput does not exceed 750 volumes of fresh gas per volume of catalyst per hour.

3. A process according to claim 1 or claim 2, in which the precipitation of the solution of the iron salt is effected at a *p*H value in the range 6.8—7.1.

4. A process according to any one of the preceding claims, in which the alkali content is in the range 3%—4%.

5. A process according to any one of the preceding claims in which from 20%—30% of the iron in the catalyst is in the elementary state.

6. A process according to any one of the preceding claims, in which the inner surface area of the catalyst is from 200—220 square metres per gram of the total iron in the catalyst.

7. A process according to any one of the preceding claims, in which the catalyst contains one or more promoters, such as lime, copper, silver and metals of the 5th to 7th groups of the periodic system.

8. A process according to any one of the preceding claims, in which the precipitation of the iron from the solution is effected with an alkali metal compound, the precipitated mass being then incompletely washed whereby, after impregnation of the mass with the alkali metal silicate, a catalyst is obtained in which the numerical value of the ratio $SiO_2:K_2O$ is less than 2.5.

9. A process according to any one of claims 1 to 7, in which the precipitation of the iron from the solution is effected by an alkali-metal compound, the precipitated mass being thereafter washed for substantially complete removal of alkali-metal compounds, the washed mass being then impregnated with an alkali-metal silicate, the alkali-metal content in the catalyst being thereafter lowered by treatment of the mass with nitric acid whilst maintaining a *p*H value of from 6.5 to 8 to yield a catalyst in which the numerical value of the ratio $SiO_2:K_2O$ is greater than 2.5.

10. A process for the production of hydrocarbons boiling in the gasoline range by the hydrogenation of carbon monoxide, substantially as hereinbefore described.

11. A process for the catalytic hydrogenation of carbon monoxide, substantially as described in the example.

12. Hydrocarbons whenever obtained by the process of any preceding claim.

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